A

Thesis

On

FABRICATION AND CHARACTERIZATION OF KAOLIN BASED MEMBRANE FOR CATALYST RECOVERY

Submitted By

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Under the Supervision of

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Certificate

This is to certify that the project report entitled, "**Fabrication and characterization of kaolin based membrane for catalyst recovery"** submitted by **Balasa Satish Kumar** in partial fulfilments for the award of Master of Technology Degree in Chemical Engineering in National Institute of Technology, Rourkela is prepared under my supervision and guidance.

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ABSTRACT

Microfiltration and ultrafiltration studies using ceramic membranes has been gaining grounds in recent times and is finding wide ranging applications in dairy, food, pharmaceutical, biological, paint, paper and water treatment industries. Choice of suitable raw materials (including binders or additives) is critical to the ceramic membrane fabrication and their performance. Conventional materials *viz*. aluminium oxide, titanium oxide and zirconium oxide have been predominantly used, owing to their high temperature stability and chemical resistance to various organic and inorganic solvents. However, as the need grows for more cost-effective resources with superior performance, efforts are made by many research groups across various labs to come up with alternate raw materials which are locally available and hence cheap and can withstand high temperature and harsh chemical environments.

In this project work, Kaolin was the primary raw material for membrane fabrication. Various additives/binders were also used based on their suitability and effectiveness in imparting special properties e.g. *mechanical strength and dispersion properties for homogeneity* to the final or finished membrane. A range of additives were used in this work and it included *boric acid, sodium metasilicate, sodium carbonate, calcium carbonate and quartz powder*. Apart from that red-mud and TiO_2 was also used to enhance the *mechanical strength* of the membrane. During membrane preparation with various stoichiometric compositions of ingredients, it was observed that higher percentages of kaolin didn't result into membranes with good flexural strength whereas increasing the % of red-mud enhanced the mechanical strength quite considerably e.g. 10.11 MPa (*membrane F*), 18.93 MPa (*membrane G*) and 12.04 MPa (*membrane H*) respectively. Methanol permeation studies showed that the average steady state flux was highest for *membrane G* (*ca*. 4.23×10^{-4} m^3 m^{-2} sec^{-1}). The fabricated membranes were characterized using standard procedures like scanning electron microscopy (SEM), field emission SEM, Powder X-ray diffraction analysis, Thermogravimetric analysis and BET surface area analysis to ascertain the membrane morphology both qualitatively as well as quantitatively. The fabricated membranes were undergone catalyst recovery study in a batch membrane module. In this work, Cu-BTC (or, HKUST-1 or, MOF-199), a well-known Metal Organic Framework (MOF) was selected as the potential catalyst based upon its superior physical properties like high surface area (*ca*. 1500 m^2 gm^{-1}) and thermal and chemical stability (*under organic medium*). Several cycles

(or batches) were carried out inside the membrane module and it was observed that *membrane G* performed better than the rest and a recovery percentage of *ca*. 61% was noted after 3 cycles before the membrane pores were completely choked. Membrane de-fouling and regeneration studies were carried out in detail using back-washing treatment inside the module itself and ultra-sonication techniques for preparing the membranes for next round of operations.

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L_h	-	Hydraulic permeability
r_l	-	Average pore radius (Using hydraulic permeability studies)
J	-	Liquid Flux across membrane
P	-	Porosity
m_D	-	Dry membrane support mass
m_w	-	Mass of the support with pores filled with water
m_A	-	Mass of the water saturated support measured in water

NOMENCLATURE

BET	-	Brunauer, Emmett and Teller
DMF	-	Dimethyl Formamide
EDX	-	Energy Dispersive X-Ray Spectroscopy
H_3BTC	-	Benzene tricarboxylic acid
HKUST	-	Hong Kong University of Science and Technology
MOF	-	Metal Organic Framework
PXRD	-	Powder X-Ray Diffraction
SEM	-	Scanning Electron Microscope
TGA	-	Thermogravimetric Analysis
RO	-	Reverse osmosis
MF	-	Micro Filtration

1. INTRODUCTION

In this chapter, a brief description on the background of this work is narrated. Introductory remarks on ceramic membranes are also highlighted. The research objectives are presented point wise along with discussion on structuring and summarizing of this dissertation.

1.1 Background of research

Microfiltration and ultrafiltration studies using ceramic membranes has been gaining grounds in recent times and is finding wide ranging applications in dairy, food, pharmaceutical, biological, paint, paper and water treatment industries. Choice of suitable raw materials (including binders or additives) is critical to the ceramic membrane fabrication and their performance. Conventional materials *viz*. aluminium oxide, titanium oxide and zirconium oxide have been predominantly used, owing to their high temperature stability and chemical resistance to various organic and inorganic solvents. However, as the need grows for more cost-effective resources with superior performance, efforts are made by many research groups across various labs to come up with alternate raw materials which are locally available and hence cheap and can withstand high temperature and harsh chemical environments.

1.2 Ceramic Membranes [1]

Ceramic membranes grew out of a need for the nuclear power industry to separate the isotopes uranium. This was achieved by utilizing Knudsen diffusion through a ceramic layer with pores in the range 6-40 nm with the emergence of new methods of separating isotopes, and the limited scope for replacement business, the companies (SFEC, Ceraver, Norton) that had developed these membranes turned their energies to non-nuclear applications. Today a number of companies market ceramic membranes. These membranes are usually of a monolithic structure. By selectivity coating the various tubes one can manifold the flows through the device. Ceramic membranes offer good thermal abrasive resistance. However, per unit surface area they are more expensive than most polymer membranes. As well as the high cost of ceramic membranes they

are vulnerable to brittle failure. The monolithic structure helps to overcome some of the handling issues, but it does represent an issue when designing a device, e.g. the sealing arrangements. Ceramic membranes are now available in zirconia, alumina, and Titania. Zirconia membrane offers the coarsest in size (microfiltration) while Titania can be made with pore in the nanofiltration range. Like their polymer brethren as the pores become finer the membranes have to be made more asymmetric. This is achieved through fabricating the membrane in a series of layers with different ceramic materials. One of the most important composite membranes is the interfacially polymerized membrane developed by Film Tec (now owned by Dow). The membrane was the culmination of more than 10 years of research, and is formed by reacting two monomers on a polysulphone support to form a polyamide coating. Another popular method of making composite membranes is by dip coating. This process involves coating an ultrafiltration membrane with a very dilute polymer solution, and then drying off the solvent. The major difficulty with this method is to choose a coating formulation that will not significantly swell the supporting structure during coating. Dip coating is also widely used to apply a protective layer on top of the membrane to protect it during manufacturing. Another layer that is sometimes required is a drainage layer. This consists of a thin coating of a highly permeable polymer, with little intrinsic selectivity. This layer is needed if the top surface of the ultrafiltration layer is of low porosity. In the late 80's, Anotec developed a ceramic membrane made by anodic oxidation of aluminum. By controlling the conditions the alumina membranes could be made within a wide range of pore sizes, and with a symmetric or asymmetric structure. These membranes are extremely fragile and have to be specially mounted so as to avoid undue mechanical stresses being applied during handling and use. One solution to the mechanical weakness of ceramic membranes was developed by Ceramesh Ltd. Their ingenious solution was to mount a zirconia coating on an Inconel wire mesh. The manufacturing process resulted in the mesh acting like reinforcing rods in concrete. As a result a ceramic membrane was made which had sufficient tensile strength and flexibility that it could be wound in to a spiral element.

1.3 Research objectives

The aim and scope of this work can be broadly summarized as:

(**a**) Fabrication and characterization of kaolin based ceramic membrane by varying stoichiometric percentage of kaolin with addition of suitable additives.

(**b**) Screening of membrane with best possible features in terms of flexural strength, permeability and continuity and crack-free surface.

(**c**) Recovery of Cu-BTC (or, HKUST-1 or MOF-199) catalyst from its mother solution selectively and studying the membrane performances

(**d**) Studying fouling and regeneration of fabricated membranes

1.4 Thesis Summary

This thesis comprises of five chapters *viz.* Introduction, Literature Review, Experimental Works, Results and Discussion and Conclusions. Each of these chapters adequately details about past and present research in similar fields, experimental methodologies followed, research findings and their possible explanations. The complete thesis has been organized as follows:

Chapter 1 introduces the field of research in brief, comprehensive description of research background and objectives of this work

Chapter 2 discusses the literature reports in detail pertaining to the field of membrane fabrication in general and ceramic membranes in specific. Various terminologies related to membranes especially on ceramic membranes are introduced and elaborated.

Chapter 3 describes the methodologies and protocols followed during fabrication of Kaolin based ceramic membrane. The macros of various experimental studies are also elaborated. Catalyst recovery experiments with Cu-BTC (or, HKUST-1 or MOF-199) from its mother solution and performance studies are also documented in detail in this segment.

Chapter 4 incorporates various results obtained during the experimental studies in including material characterization. The possible explanation to various observations made during experimentation is also incorporated here.

Chapter 5 summarizes various findings of this project work and possible future scope of this work is also explained.

2. LITERATURE REVIEW

In this chapter a detailed description on the basics of membrane science and technology have been highlighted. Various terminologies related to membranes especially on ceramic membranes are introduced and elaborated. Numerous applications which have shown promise using ceramic membranes are discussed as well.

2.1 Composite Membranes

The major problem with asymmetric reverse osmosis membranes is that one material has to carry-out all the functions e.g. separate, support, and protect. It therefore seems only natural to try making a membrane from layers of different material designed for each function rather a compromise material for all functions.

In the late 70's Monsanto were developing polysulphone membranes for gas separation. The membrane structure was similar to the cellulose reverse osmosis membrane but made from polysulphone. The major problem though was to achieve the permeability required meant that the dense film had to be very thin, and in manufacture this led to defects which have a profound effect on performance. Monsanto overcome this problem by over coating the membrane with a coating of highly permeable polydimethylsiloxane (PDMS). The coating process plugged the defects and it is readily shown that while the coating has only a marginal effect on the defects, and hence substantially improves the selectivity. One of the most important composite membranes is the interfacial polymerized membrane developed by Film Tec. The membrane has the culmination of more than 10 years of research, and is formed by reacting two monomers on a polysulphone support to form a polyamide coating

Another popular method of making composite membranes is by dip coating. This process involves coating an ultrafiltration membrane with a very dilute polymer solution, and then drying off the solvent. The major difficulty with this method is to choose a coating formulation that will not significantly swell the supporting structure during coating. Dip coating is also widely used to

apply a protective layer on top of the membrane to protect it during manufacturing. Another layer that is sometimes required is a drainage layer. This consists of a thin coating of a highly permeable polymer, with little intrinsic selectivity. This layer is needed if the top surface of the ultrafiltration layer is of low porosity.

2.2 Homogeneous Microporous Membranes

These are a large number of micro porous membranes, made by a variety of processing methods .each product has found a number of niche markets. PTFE membranes are widely used in laboratory work on account of their inertness. On The large industrial scale the stretched polypropylene membranes of Enka and Memcor found the widest application.

Table 2.1: Some of the homogeneous microporous membranes, methods manufacturers

Manufacturer	Materials	Technology
Nuclepore	Polycarbonate	Track-Etch
Gore	Gortex-PTFE	Stretching
Enka	Accurel-PolyPropylene	Stretching
Memcor	Polypropylene	Stretching
Gelmans Science	Repel-Polyacrylic	Photopolymerisation

2.3 Asymmetric membranes

The most common method of manufacturing asymmetric membranes is known as solution phase inversion. The process consists of dissolving a polymer in a suitable solvent, and then casting this on to a cloth. After a small time the cloth and then attached polymer solution film are quenched in water .water diffuses in to the cast film which becomes thermodynamically unstable and expels the now non solvent to create a honeycomb structure. The effect of water is to create an unstable polymer solution that phases separates. It is the nature of this process that creates the detailed microstructure. By carefully selecting the solvents and adjusting the time the cast membrane sees air before it quenches the asymmetry and structure of the membrane can be controlled.

Some degree of asymmetry is absolutely essential to make reverse osmosis work, since the key separating layer has to be extremely thin. The remainder of the material is there to provide mechanical support and allow one to physically handle the material. If the wrong side of the membrane is presented to the feed there would be severe polarization due to the stagnant layer of liquid trapped in the membrane. While the support layer is there to provide mechanical support for the separating layer it can have some impact on the permeability. Pressure lost in the sub-structure reduces the permeability of the membrane, and in the case of reverse osmosis it also serves to reduce the separating power. Conversely, if the support structure is very porous it means that defects in the separating layer can become more significant. In other words the sub-structure throttles the effect of defects in separating layers. In other words the sub-structure throttles the effect of defects in separating layers. Thus it can seen that there us a practical element to balancing various features in the membrane structure.

2.4 Membrane Technologies

2.4.1 Introduction

Membrane technology is used across a whole range of industries. There is no single membrane type at the root of these applications, nor a single technology. However, specific applications and developments have fuelled its growth and provided the seeds for subsequent opportunities .For example the early 60's saw the emergence of reverse osmosis for the desalination of sea water. Once created it was not long before a vast range of additional applications emerged, from improving the clarity of ice crystals, to dewatering of fruit juices. The 1990'shas brought the environment and water quality as key drivers for the advancement of membrane separation technologies, and with it the interest in water reuse and product recovery processes.

2.4.2 The Driving Forces of Separation

For processes like crystallisation, Adsorption, the separation achieved is related to the thermodynamic stability, with kinetic serving to dictate the time and size of plant are required. In contrast for membrane processes separation is determined by the relative kinetics of permeation, with thermodynamic providing the scale and size of plant are required.

Irreversible thermodynamics provide the frame work for understanding membrane separations. The driving force for separation comes from gradients in thermodynamic variables. Commercial separation processes are governed by the differences in one or more thermodynamic factors

- Pressure
- Concentration
- Electric potential
- Temperature

That exists between two phases being separated by the membrane. In response to these factors there are flows of mass, heat and electricity. At a local level the relationship between the forces,

2.4.3 Purification, Concentration, Fractionation

Membranes are used for

- Purification
- Concentration
- Fractionation

Typical examples of purification occur in the fine chemical and pharmaceutical industries where membranes are used to purify products by purging low molecular contaminants through the membrane. An "inverse'' example that is carried out in the food industry is to use a membrane to retain the heavier colloidal components and give ''clear'' permeate product. The result is a product with a longer shelf life.

In effluent applications membranes are used to concentrate waste products, and hence reduce the volume to be shipped and disposed. In recovery applications such as in the paint industry membranes are used to concentrate the product to a level either sufficient for selling or to allow it to be recycled.

Membranes do not usually provide a sharp separation based on molecular weight. However, the fractionation that can be achieved is sufficient for its wide use in the processing of biological fluids, e.g. blood

2.5 Membrane Materials & Membrane Structure

2.5.1 Introduction

In reading the research and patent literature one might think that any material can be made into a membrane. Fortunately most such membranes academic rather than commercial value. Nevertheless, the number of materials that are available is large, and viable membranes can be made from polymers, ceramics, and metals. This variety stems from the fact that there is no such thing has a perfect membrane material. One membrane material might be the best for one application but hopeless at another. For a membrane to be viable it must not only have the necessary performance properties but also satisfy a number of secondary properties

Membranes come in a wide range of forms, and structures. While many materials come in more than one form there is frequently a processing reason which can make it difficult to obtain a particular material in a desired format. At the macro scale there are three main forms

- Flat sheet
- Hollow fiber
- Tubular

Tubular membranes differ from hollow fiber only in that their larger diameter means that they have to be supported. Other variants, such as reticulated surfaces to encourage mass transfer, have been investigated but remain at the margins of the commercial world with their interest being essentially a scientific one.

2.5.1.1 Dense Films

The simplest structural type of membrane is the dense polymer film. Such materials are nearly exclusively of the ion exchange type and are used in electrically driven or dialysis type processes.

Electro dialysis uses dense films of anion and cation exchange polymers. These membranes were based on cross linked styrene-divinyl benzene chemistry with the negative charge being introduced by sulphonic or carboxylic acid groups. Anion membranes were available based on

aliphatic chemistry with the positive charge being introduced through quaternary ammonium group

2.5.2 Pressure Driven Processes

The principles involved in pressure driven processes are elaborated in the following paragraphs.

2.5.2.1 Filtration Processes

In value terms, filtration processes are the most important group of membrane processes for industrial users. At the top end of the scale there is microfiltration which deals with particles at the boundary of visibility, such as biological cells. Despite being the oldest of the filtration technologies, microfiltration is perhaps the least mature, and offer great potential. At the other end of the scale there is reverse osmosis which deals with the separation of ions and small molecules from water. Historically, reverse osmosis has been called hyper filtration, but the term reverse osmosis reflects the fact that there is frequently a significant thermodynamic component to be overcome in the separation. In-between their lies the processes of ultrafiltration and nanofiltration. The former is principally concerned with separation of macromolecules ranging from molecular weights of a few thousand to a million, and in market terms has the largest value. The latter is concerned with the separation of small low molecular weight non-volatile organics from water.

Table 2.2: Characteristics of filtration processes

Process Technology	Separation Principle	Size range
Microfiltration	Size	0.1µm-1 µm
Ultrafiltration	Size, charge	1 nm -100 nm
Nanofiltration	Size, charge, affinity	~1 nm
Reverse osmosis	Size, charge, affinity	<1 nm

In keeping with the different uses the various membrane technologies are characterized in different ways. Microfiltration membranes are characterized in terms of pore size, while ultrafiltration membranes are normally described in terms of a molecular weight cut off.

As might be expected the operating parameters for these filtration processes vary drastically, with microfiltration processes offering a high recovery of feed at low pressure, while reverse osmosis offers lower recoveries at much higher pressures

Table 2.3: Typical operating parameters and Membrane Materials used for pressure driven processes

Process Technology	Material	Typical Operating range		Rejected Species
		Pressure (bar)	Recovery	
Microfiltration	Polymers Ceramics Metals	0.5-2	90-99.99	Bacteria, Spores, Cysts
Ultrafiltration	Polymers Ceramics	1-5	80-98	Proteins, Viruses, Endotoxins, pyrogens
Nanofiltration	Polymers	3-15	50-95	Sugars, Pesticides
Reverse osmosis	Polymers	10-60	30-90	Salts, Sugars

Membrane Separation Processes are used to concentrate constituents, extract water, and exchange electrolytes. Fractionation is possible, though sharp selection on the basis of molecular weight is not a characteristic of membranes. However it is sufficiently sharp to provide a useful separation in the case of blood, where the blood is retained and low molecular weight materials pass through the membrane.

Along with the change in particle size separation goes a change in basic characteristics of devices. The essential feature in going from RO to MF is that the characteristic dimensions of the devices become larger, as do the cross flow velocities, and fluxes

Table 2.4: Typical dimensions and conditions in membrane filtration devices

Technology	Distance between membranes (cm)	Cross flow velocity (cm/s)	Flux ($L/m^2/hr$)
Ultrafiltration	0.05	10-25	40-90
Nanofiltration	0.1	25-100	50-100
Reverse osmosis	0.15	100-300	100-200

2.5.2.2 Ultrafiltration

One of the first major uses for ultrafiltration on an industrial scale was in the concentration of paint that had been rinsed off cars during initial stages electrophoric painting. This technology is now the established method of providing the primary coat of paint on cars. From this base UF is now used in an ever increasing range of food processes. Traditional separation processes like evaporation and freezing denature proteins and hence, alter the flavor and taste of food products. In contrast membrane processes can operate at ambient or any desired temperature at which the membrane is thermally stable. This makes membranes a particularly attractive method of separation in the food and beverage industry. In single process organisms and large macromolecules, which contribute to haze, can be can be removed and produce a clear cold sterilized product. UF is now widely used in the food and beverage industry. Environmental pressure has focused interest in effluent treatment. Particular interest has been in effluents which contain hazardous or valuable products. Membranes have been used to recover and concentrate products. In some cases, the recovered as part of this process can also be reused, giving the additional benefit of reducing water demand. Even where the material recovered has no intrinsic

value, concentration of it can make other treatment processes more viable, and reduce the volume of waste to be transported, and there by provide a cost saving.

2.5.2.3 Microfiltration

As a laboratory tool microfiltration has a long established history. As a process tool it is far less mature. It has got the widest use in clarification processes where a key aspect is frequently the "dirt-holding" capacity. Recently though water quality requirements have driven interest in microfiltration for treating water to remove chlorine resistant pathogen. Fouling mechanism and regeneration of two asymmetric microporous Al_2O_3 microfiltration membranes for the recovery of titanium dioxide particles in acid waste streams were investigated [2]. Porous Ceramic membrane reactor has promising method to solve the problem concerning catalysts separation from the reaction mixture and make the production process continuous in heterogeneous catalysis [3] Natasa Zabukovec Logar and Venceslav Kaucic did illustrate the storage of hydrogen in waste water treatment by using Nano porous materials. Inorganic solids have greater utility in catalyst because of their larger internal surface area applications emphasizing catalysis, hydrogen and energy storage [4]. Ceramic membranes were prepared using clay. To this they had added sodium carbonate, sodium metasilicate, calcium carbonate. By adding these chemicals a high flux ceramic microfiltration membrane was prepared and they removed chromate ions from the aqueous solution of micellar flocculation [5]. Low cost ceramic membranes were prepared by using inorganic precursors. By using the robust ceramic membranes they had successfully separated mosambi juice (using microfiltration method) [6]. Some literature also reported fabrication of low cost ceramic membrane using kaolin, quartz powder, calcium carbonate following uniaxial compaction method and it was used to separate oil from oil-water emulsion and bacteria from bacterial broth [7]. In another article, fabrication of low cost ceramic membrane was reported using kaolin, ball clay, quartz powder, calcium carbonate, feldspar, pyrophyllite as the raw materials and paste casting technique was followed. Additionally, titanium dioxide was added to the mixture. By adding titanium dioxide it was observed that the flexural strength of the membrane increased it was successfully used to separate oil droplets from Bovine Serum Albumin (BSA) solution [8]. Ceramic membrane was prepared by using polydimethylsiloxane (PDMS) is ceramic hollow fiber support this ceramic hollow fiber is coated on the ceramic membrane is such that high quality ceramic hallow fiber PDMS composite

membranes were fabricated for recovery of biobutanol [9]. In another study, composite ceramic membrane was prepared using Pd-layer which was supported onto Al_2O_3 and was used for the recovery of methanol. The main advantage of this work was 85% recovery of methanol [10]. Another research group had successfully recovered iron (III) catalyst from aqueous streams by using ultrafiltration technique applying ceramic membranes [11]. Literature was also found on preparation of porous ceramic membranes by using titanium dioxide. It was coated with Ti-Mn catalyst layer on top surface of the membrane. The main application of this work was to enhance water treatment [12]. Ceramic membranes were also prepared by using calcium carbonate, sodium metasilicate and titanium dioxide and were used to separate Iodine from Brine Water [13]. Some research groups had also shown the effectiveness of ceramic membranes for separating biodiesel where calcium glyceroxide was used as a catalyst [14]. Researchers had also designed and prepared chemical process membrane reactor (CMR) by adopting superior metal catalyst for H_2 gas production and separation from the other constituents [15]. Destruction of coalescer filters by coke particles was a very important area faced by polyolefin units of petrochemical plants. A lot of fund and time was wasted for reclogging/substituting the coalescer filters. In an article it was reported that γ-Al_2O_3 based ceramic microfiltration membrane could be effectively utilized to get rid of coke particles from petrochemical wastewaters before introducing to the coalescers [16]. Various other research works had reported the successful fabrication of membranes using carbonaceous materials having wide ranging applications in catalyst recovery within the microfiltration regime [17-19]

2.6 Different material characterization methodologies and their working principle

In the following paragraphs the working principle of several instruments used in this work for material characterization both qualitatively as well as quantitatively are explained in detail. The methods are: Scanning Electron Microscopy (SEM), Powder X-ray diffraction analysis (XRD), BET Surface Area Analysis and Thermogravimetric Analysis (TGA).

2.6.1 Thermo gravimetric analysis

Thermal Gravimetric Analysis or Thermo gravimetric Analysis (TGA) is an essential laboratory technique which is employed to predict the thermal stability of material by measuring the change of weight with respect to increase in temperature in controlled atmosphere. Based on the data

obtained like weight loss, temperature and rate of temperature change, the information on absorbed moisture, proportion of organic and inorganic materials in sample, and solvent residue apart from degradation temperature is obtained after performing required transformation of the results for interpretation. Normally TGA can be conducted either in atmospheric environment or inert environment using nitrogen gas in pre-programmed gas flow rate. The heat flow change is also monitored to obtain differential scanning calorimetery data used for calculating enthalpy of reaction. The experimental procedure involves placing a known weight of sample in a crucible kept on high precision sample which resides in a furnace. The temperature is gradually raised to our requirement and cooled down to room temperature and .the data acquisition system automatically plots the relation between temperature and weight loss which is finally smoothened to find the exact point of inflection. Derivative weight loss curve can identify the exact point of maximum weight loss and the temperature which indirectly provides degradation profile of the sample.

2.6.2 BET Surface Area Analysis

In 1938, Brunauer, Emmett and Teller (BET) introduced a new concept into the field of surface science which describes the multi-layer adsorption of gases over surfaces. This theory was later exploited to estimate the total surface area of material and is given by equation

$$\frac{x}{v\,(1-x)} = \frac{1}{cv_{mon}} + \frac{x(c-1)}{cv_{mon}} \qquad (2.1)$$

Where x is relative pressure P/P_0, v is the STP volume of adsorbate, v_{mon} is STP volume of the amount of adsorbate required to form a monolayer, c is the equilibrium constant.A key assumptions used in development of BET equation is that the formation of multi adsorption layers unlike Langmuir theory (assumes monolayer adsorption of gases) and that successive heats of adsorption for all layers except the first are equal to the heats of condensation of the adsorbate. It also assumes that no multilayer formation occurs until monolayer adsorption of entire sample is completed. Another critical assumption is that there are no lateral interactions between adsorbed molecules. Hence, BET model describes the process of physisorption better than the Langmuir theory although it is generally still not a good model for adsorption on micro porous materials. Micropores are not covered under this model as BET equation over estimates the surface area of microporous materials.

In a typical experiment, the sample to be analyzed is pre heated to remove maximum moisture. A known weight of dried sample is first known in the sample tube of known volume for a process called outgassing. Outgassing is performed in outgasser port of equipment prior analysis in order to completely remove the moisture and gases already adsorbed in the micro and nano pores present sample. This outgassed sample is weighed and then employed for analysis in analysis port. Nitrogen gas is often used for analysis because of its well established molecular size, inert nature, availability in high purity and reasonable cost. The entire sample tube is immersed in a coolant bath of liquid nitrogen exposing it lower temperature. At this point, a purge of nitrogen gas is introduced into the sample tube, which slowly gets adsorbed on the sample surface. The relative pressure of nitrogen is recorded against the volume of adsorbate and finally surface area of sample is estimated. All the operations are computer programmed using software supplied with equipment

2.6.3 Scanning Electron Microscopy

Scanning Electron Microscope (SEM), as the name suggest is an electron microscope which provides the detailed information regarding sample's surface morphology, composition and other surface properties such as electrical conductivity. A high energy electron beam is directed towards the sample surface which interacts with the atoms that make up sample, and produce secondary electrons, back scattered electrons, characteristic X-rays, light, specimen current and transmitted electrons which is detected with the help of special sensors to give high resolution images of sample surface morphology. When the high energy electron beam interacts with the electrons present in the sample, X-rays are emitted in this process, and these are used to identify the composition. It also measures the abundance of elements in the sample; characteristic feature of X-ray emitted depending up on the sample composition. The X-rays generated are mainly concentrated from a region 2 μm depth and hence EDX cannot be termed as purely a surface science technique.

The physical working of SEM involves, an electron beam being emitted from an electron gun, which is fitted with a tungsten filament cathode. Tungsten is used because of its highest melting point and low cost. The electron beam is condensed by one or two condenser lenses. When primary electron beam interacts with the sample, electron loses energy by repeated random scattering. The energy exchange between the electron beam and the sample, results in the

reflection of high energy electrons, emission of secondary electrons and the emission of electromagnetic radiation, which can be detected, and so also the beam current absorbed by the specimen. This is used to create images of the specimen surface.

2.6.4 Powder X-Ray Diffraction analysis

X-ray diffraction technique is powerful characterization tool which provides information about the crystal structure, and physical properties of crystalline materials and thin films. In this technique, the scattered intensity of an X-ray beam generated upon hitting the sample is measured as a function of incident angle, scattered angle, polarization, and wavelength and as pointed out by A. W Hull [20] in paper titled "A New Method of Chemical Analysis" that "Every substance produces a pattern, same substance produces always same pattern and in a mixture of substances each produces its pattern independently of the others". Thus XRD patterns serves as a finger print of the each material.

In a typical analysis procedure of XRD machine, the sample is mounted on a goniometer and is gradually rotated with simultaneous bombardment of X-rays which after hitting the sample diffracts into different angles to generate two dimensional images at different positions. This data is integrated to obtain three dimensional data using mathematical method of Fourier transform, combined with the chemical data of the sample.

Although scattering of beams from the sample leads to destructive interference, there are specific directions in which they add up to give diffraction pattern governed by Bragg's Law given by

$$2d \sin\theta = n\lambda \qquad (2.2)$$

whereθ is the incident angle, d is the spacing between the planes, n is any integer and λ is the wavelength of incident beam. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

2.7 Use of various raw materials and additives/binders applied in this work

Various additives are used in this work to impart special properties to the finished membrane. They include:

$CaCO_3$ *is used for porosity controlling agent*.

Na_2CO_3 *improves dispersion properties and thereby creating homogeneity*.

Boric acid *increases mechanical strength by creating meta borates by sintering at high temperature*.

Sodium metasilicate *increases mechanical strength by creating silicate bonds*.

Red mud *is composed of mixture of solid and metal oxide bearing impurities. It is solid waste product of Bayer process and hence useful*.

Quartz Powder *is chemical compound consisting of one part of silica and two parts of oxygen. Addition of quartz powder increases the mechanical strength*.

Titanium dioxide *is known for high thermal stability and chemical inertness*.

Kaolin *is known for its insolubility in Water. It is stable and chemically unreactive under ordinary conditions*.

2.8 Hydraulic Permeability studies

Hydraulic Permeability or Conductivity represents the ease with which water permeates through the porous media particularly through rocks or soil. It largely depends on the intrinsic permeability of material and degree of saturation of media. The hydraulic studies of clay supports (both normal and HCl treated supports) were carried out using the standard membrane module. Distilled water was used for all the experiments.

Hydraulic permeability (L_h) and average pore radius (r_l) of membrane were determined using equation suggested by Almandoza et al. [8]

$$J = \frac{n\pi r^4 \Delta P}{8\mu l} = L_h \Delta P \qquad (2.3)$$

where, J is the liquid flux ($m^2\ m^{-2}\ s^{-1}$), ΔP is the transmembrane pressure (in kPa), μ is the viscosity of water and l is the pore length (assumed as membrane thickness). Considering porosity of sample as $\varepsilon = n\pi r^2$, Equation **(3.1)** changes to

$$r_l = \left[\frac{8\mu l L_h}{\varepsilon}\right]^{0.5} \quad (2.4)$$

Porosity was figured out using the principle of Archimedes' [] given by Equation

$$P = \frac{m_W - m_D}{m_W - m_A} \quad (2.5)$$

Where, m_D is the dry support mass, $m_w$is the mass of the support with pores filled with water (pores are filled with water under vacuum), m_A is the mass of the water saturated support measured in water (A refers to Archimedes'), and *P* is the porosity.

All the experiments were performed at room temperature and pressure maintained at 300 kPa. Membrane support was fixed tightly using commercially available epoxy resin '**silicon sealant'** to groove membrane plate. A very high flux was observed at the initial stages but reduced gradually to steady state value with time due to compaction of membrane. Permeate volume with respect to time was noted down to study flux variation and the steady state flux was used to calculate the hydraulic permeability and estimate pore radius.

3. EXPERIMENTAL WORKS

In the following paragraphs, detailed experimental methodologies and protocols on membrane fabrications, catalyst synthesis and catalyst recovery are elaborated.

3.1 Fabrication of Kaolin based membranes

Kaolin-based membrane support was prepared following the standard method described elsewhere [8]. The membranes were prepared by paste casting method. Membranes were fabricated by using varying compositions of Kaolin and other additives or binders as described in **Table 3.1**. A stoichiometric proportion of various raw materials were mixed thoroughly using distilled water and a uniform paste was prepared. Later on, the paste was casted on a solid surface and was moulded in the shape of discs with uniform dimensions. Then the casted membranes were initially dried at ambient conditions for 24 hours. Then the membranes were shifted to a high temperature muffle furnace and carefully stacked on a grooved solid base so that both sides of the membranes were heated uniformly, reducing the chance of deformation and uneven thermal expansion. The membranes were then sintered in two different ramps. Firstly, they were heated at 473 K for 2 hours and cooled subsequently inside the furnace before finally exposed to a very high temperature of *ca*. 1223 K for 6 hours before being cooled down to room temperature. A sintering temperature of 950^{o}C or 1223 K was chosen after some trial and errors with various raw materials. Finally, the sintered membranes were nicely polished using Silicon Carbide abrasive paper (C-180) to give the membranes fine textural properties and aesthetic look.

The membrane strength was then tested using Universal Strength Testing Machine. The flexural strength or breaking limit of the fabricated membranes was one of the several factors based upon which membranes were selected for catalyst recovery experiments. Although several membranes were fabricated but many could not surpass the standard benchmark and wasn't further used.

Table 3.1: Compositions of fabricated membranes

Sl. no	Membranes	Kaolin (wt %)	TiO_2 (wt %)	$CaCO_3$ (wt %)	Sodium carbonate (wt %)	Boric acid (wt %)	Red mud (wt %)	Sodium metasilicate (wt %)	Quartz powder (wt %)
1	**A**	85.79	--	--	7.396	3.25	--	3.55	--
2	**B**	42.89	42.89	--	7.39	3.25	--	3.55	--
3	**C**	42.89	21.44	21.44	7.39	3.25	--	3.55	--
4	**D**	40.62	8.39	20.31	6.99	--	--	3.35	20.31
5	**E**	20	5	15	--	5	20	5	30
6	**F**	20	5	15	--	5	25	5	25
7	**G**	20	5	15	--	5	30	5	20
8	**H**	20	5	15	--	5	45	5	5

Membranes (A-H) were prepared by using paste casting method. Here, at first we took stoichiometric proportions of various chemicals as mentioned in Table 3.1 and mixed them properly. Then we added sufficient water (as required) and mixed them thoroughly. Later on, the paste was transferred into the paste casting module where the membranes were casted according to predetermined size and thickness.

3.2 Synthesis of Cu-BTC catalyst (or, HKUST-1 or MOF 199)

Cu-BTC or HKUST-1 was synthesized hydrothermally following the procedure explained by Chui et al. [20].1, 3, 5-benzenetricarboxylic acid (1.0 g) was dissolved in 30 ml of a 1:1 mixture of ethanol/*N*, *N*-dimethylformamide (DMF). In another flask, Copper (II) Nitrate trihydrate

(2.077 g) was dissolved in 15 ml water. The two solutions were then mixed and stirred for 10 min. They were then transferred into Teflon-lined stainless steel autoclave and heated at 373 K for 10 hours. The reaction vessel was cooled to room temperature normally. The resulting blue crystals were isolated by filtration and extracted to remove solvated DMF. The product was then dried at room temperature.

3.3 Characterization

Characterization of samples (i.e. HKUST-1, kaolin membranes) was carried out systematically. The prominent characterization techniques that were adopted for analysis were SEM, FESEM, XRD, BET and TGA analysis. The images, for studying the membrane surface morphologies were taken via Scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDX) (JEOL JSM-6480 LV). The samples were gold-coated for a better conductivity, facilitating the imaging process. The crystalline phase of the Cu-BTC catalyst (or, HKUST-1) and Kaolin based ceramic membranes were determined using an X-ray diffractometer (Philips Analytical, PW-3040) equipped with the graphite monochromatized CuKα radiation (λ=1.5406 Å) in 2θ angles ranging between $5^o<2\theta<75^o$ at room temperature. BET surface area analysis was performed by BET surface area analyzer (Autosorb-1, Quantachrome). The relative pressure in BET surface area calculation was programmed between 0.1-0.33. Thermal stability of samples was carried out in detail in a TGA apparatus, Shimadzu (DTG 60 H).

3.4 Permeation Study and recovery of catalyst using Kaolin based Membranes

Methanol permeation studies were carried out in order to ascertain the permeability properties of kaolin membranes. Methanol was primarily used for calculating the flux rate. The pressure gauge used was pre-calibrated and prior to carrying out any permeation study, testing for any leakage in the membrane module was carried out using soap solution. During various experiments carried out with kaolin membrane, a standard pressure of ~ 3 kg/cm^2 was found to be suitable (lies within the microfiltration regime). Methanol was pressurized through the membrane in the filtration module and corresponding flux rate was calculated at specified intervals of time.

Based upon suitability in physical properties, the fabricated membranes were screened for catalyst recovery experiments. In this work, *membranes G and H* were found to be the most promising based upon their superior physical strength, permeability and continuity in their structure and were further used for application study.

Initially, Cu-BTC was dispersed in Methanol and a suspension was prepared by taking a known quantity of catalyst (HKUST-1), mixed at high speed with magnetic stirrer, followed by ultra-sonication. The suspension was then transferred into the stainless steel membrane module and pressurized through the membrane and corresponding flux rate was calculated at specified intervals of time and the process was continued till the permeate flow completely stopped.

Once a cycle was finished, the membrane was removed and its orientation to the flow was reversed for performing **Back Wash** operation. It was carried out at pressure slightly greater than 3.5 kg/cm^2 with fresh methanol and permeate containing catalyst was collected, filtered and then dried, and finally weighed from which recoverability was calculated (details of which is documented in Results and Discussion section).

Once **Back Wash** operation was completed, the membrane was again reversed and methanol permeation studies were carried out in order to ascertain the change in permeability properties of the kaolin membranes. This operation mentioned above (such as permeation with catalyst suspension via back wash operation followed by methanol permeation) loops to form a cycle. Finite number of cycles was carried out on a single membrane module until **Back Wash** operation yields no alteration in permeate flow (say clogging of membrane by catalyst).

The above experimental procedure was carried out on *membranes G and H* whose catalyst recovery percentages were determined.

3.5 Experimental setup

The methanol permeability and catalyst recovery experiments for Kaolin membranes were carried out using the following experimental set up as shown in Figure 3.1. As is clearly shown in the figure, the experimental set up comprises of two major parts *viz.* membrane module and compressor section.

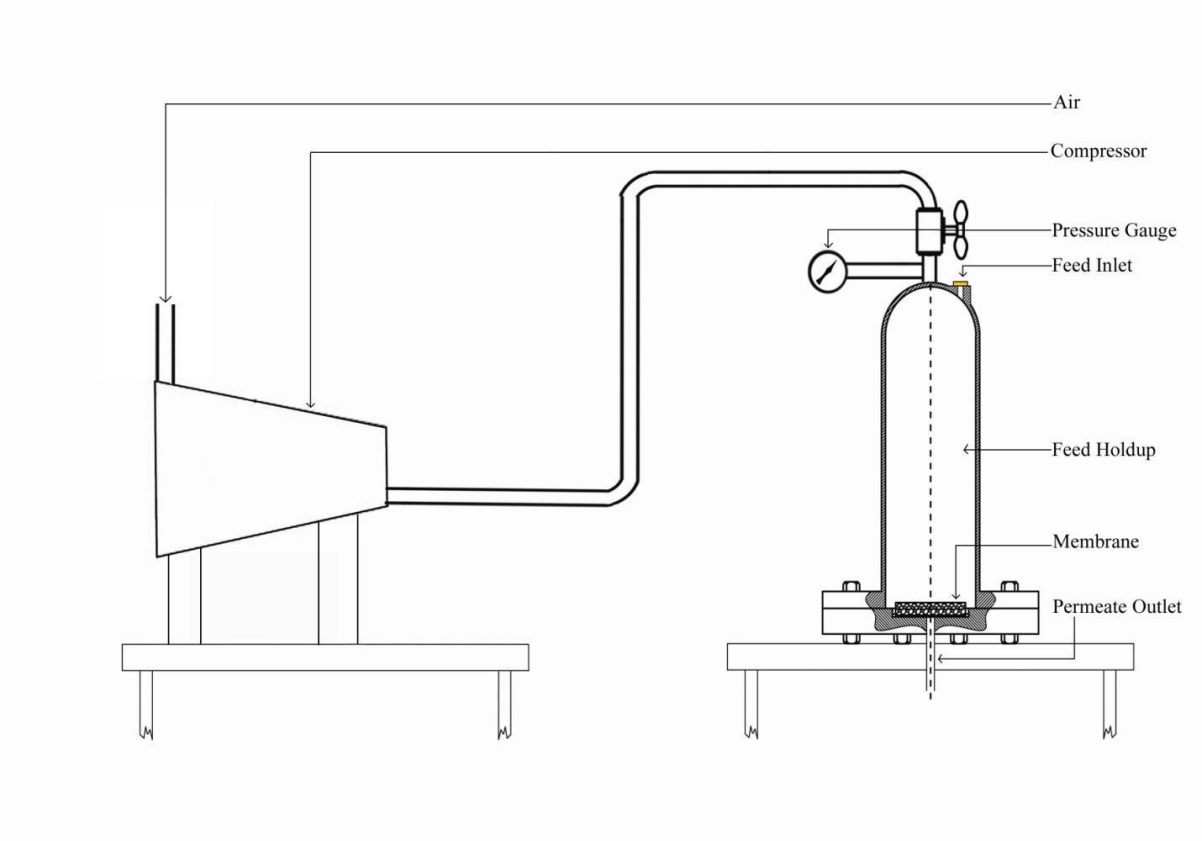

Figure.3.1 Schematic Diagram of the Experimental set up for permeation and catalyst recovery studies

3.5.1 Membrane Module

The home made membrane module is made of stainless steel and it consists of two sections: *feed hold up section* and *grooved membrane holding plate*, with extended flanges bolted tightly together. *Feed hold up section* is a hollow cylindrical portion capable of holding 300 ml of feed per batch. At the top of the cylinder there is an inlet port for introducing feed. The compressed air is regulated via a valve and is used to pressurize the feed solution. A calibrated pressure gauge is fitted into the module to indicate the air pressure exerted into the system.

Membrane holding plate is a circular disk, designed to hold membrane tightly during the process. It consists of concentric circular grooves (Figure 3.2), with a provision to incorporate an 'O' ring, which eventually helps to arrest the possible leakage upon pressurizing the system. The flanges holding both parts are tightened with 'nut and bolt' arrangement in order to lock the system properly and leak proofing it.

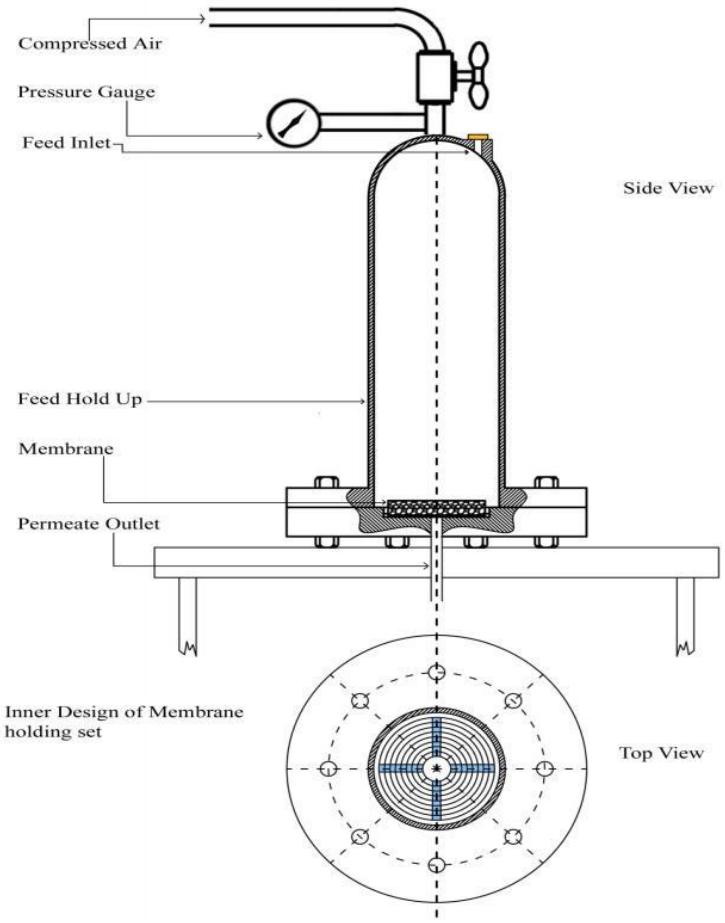

Figure.3.2 Side view and Top View of Membrane Module

3.5.2 Compressor Section*:* Compressor, as shown in Figure 3.1, supplies compressed air into the membrane module, hence pressurizing the feed to the required level. The pressure gauge monitors the system pressure and the system pressure is adjusted using the valve.

4. RESULTS AND DISCUSSION

In the following paragraphs, a comprehensive analysis of various observations made during the experimentations is elaborated. The results include various characterizations of the fabricated membranes as well as catalyst along with permeation study and catalyst recovery results.

4.1 Scanning Electron Microscopy and Field Emission SEM Imaging

SEM and FESEM images of the kaolin based membranes are shown in Figure 4.1. The images include various membranes fabricated at different stoichiometric compositions in Kaolin and other additives (*the details of which is given in table 3.1*) and exposed to the same thermal and mechanical treatments. All other images, excluding (Figure 4.1 (A), (B) and (C)), it is very clear that a decrease in Kaolin percentage and an increase in percentage of red-mud, leading to the membrane fabrication, increases the surface roughness and unevenness. The porous network of the structure also gets affected during the process. However, an increase in flexural strength to *ca*. 18.9 MPa largely circumvents the limitations, since the membranes can be effectively used in high pressure systems. A systematic analysis of the images also reveals the fact that perhaps paste casting method might not yield as smoother a surface as is possible in other moulding/casting methods.

4.2 Powder X-ray Diffraction Analysis

Figure 4.2 shows the powder XRD patterns of various fabricated membranes. The powder X-ray diffraction patterns corroborates well with the findings on surface morphology. The major peaks are identified based on the information available from database. Regular peaks are identified for sintered kaolin membranes using PDF-2 database of X'pertHighScore 1.0 software. Presence of *Quartz, Kaolinite, Silica and Titania* are the typical peaks observed in all the membranes. From Figure 4.2, it may be concluded that membranes undergo phase change and crystallinity especially with an increase in sintering time and temperature, leading to an increase in the mechanical strength as well.

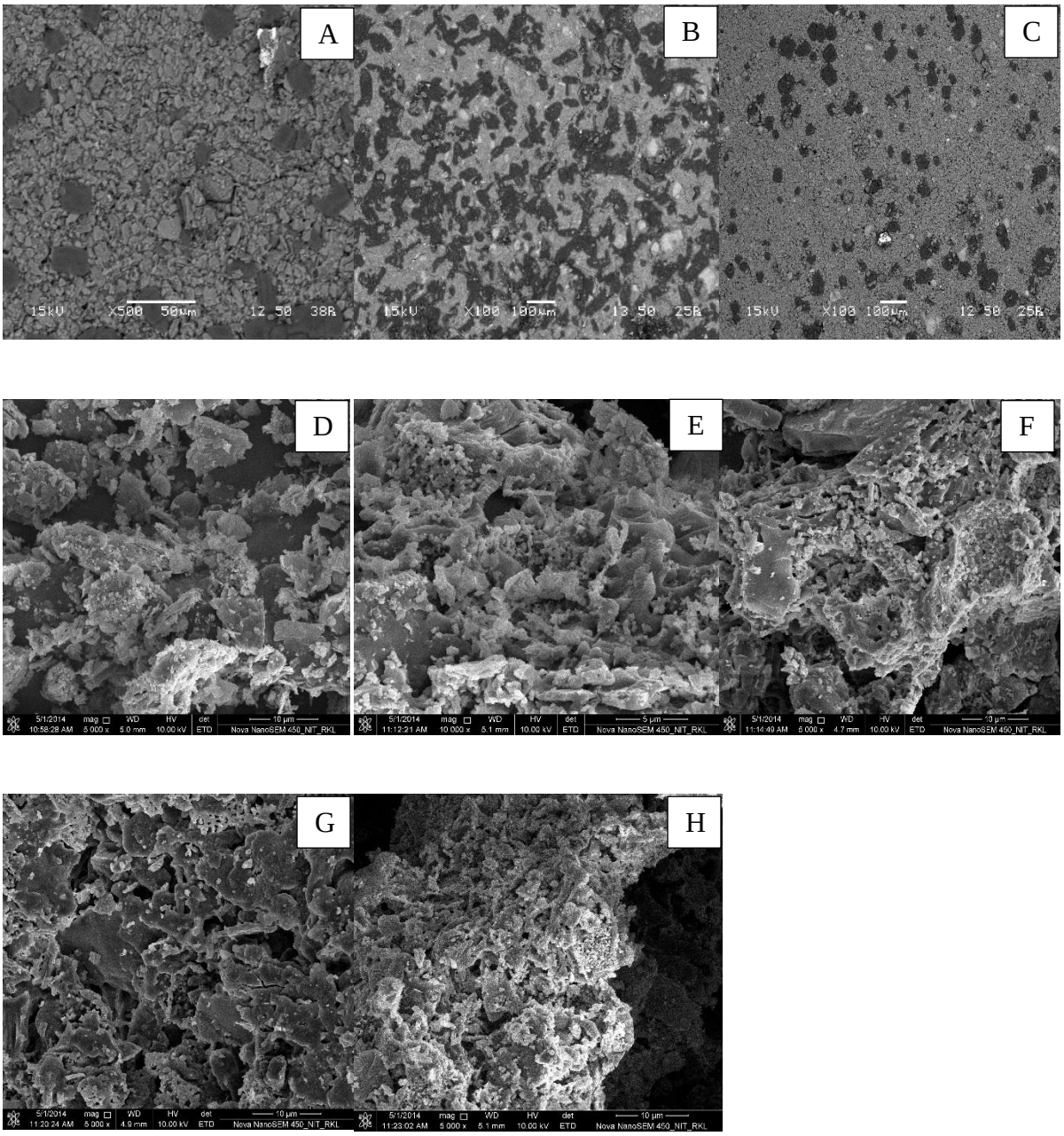

Figure 4.1: SEM images of fabricated membranes [A – C] and FE-SEM images of fabricated membranes [D – H], post sintering at 1223 K for 6 hrs

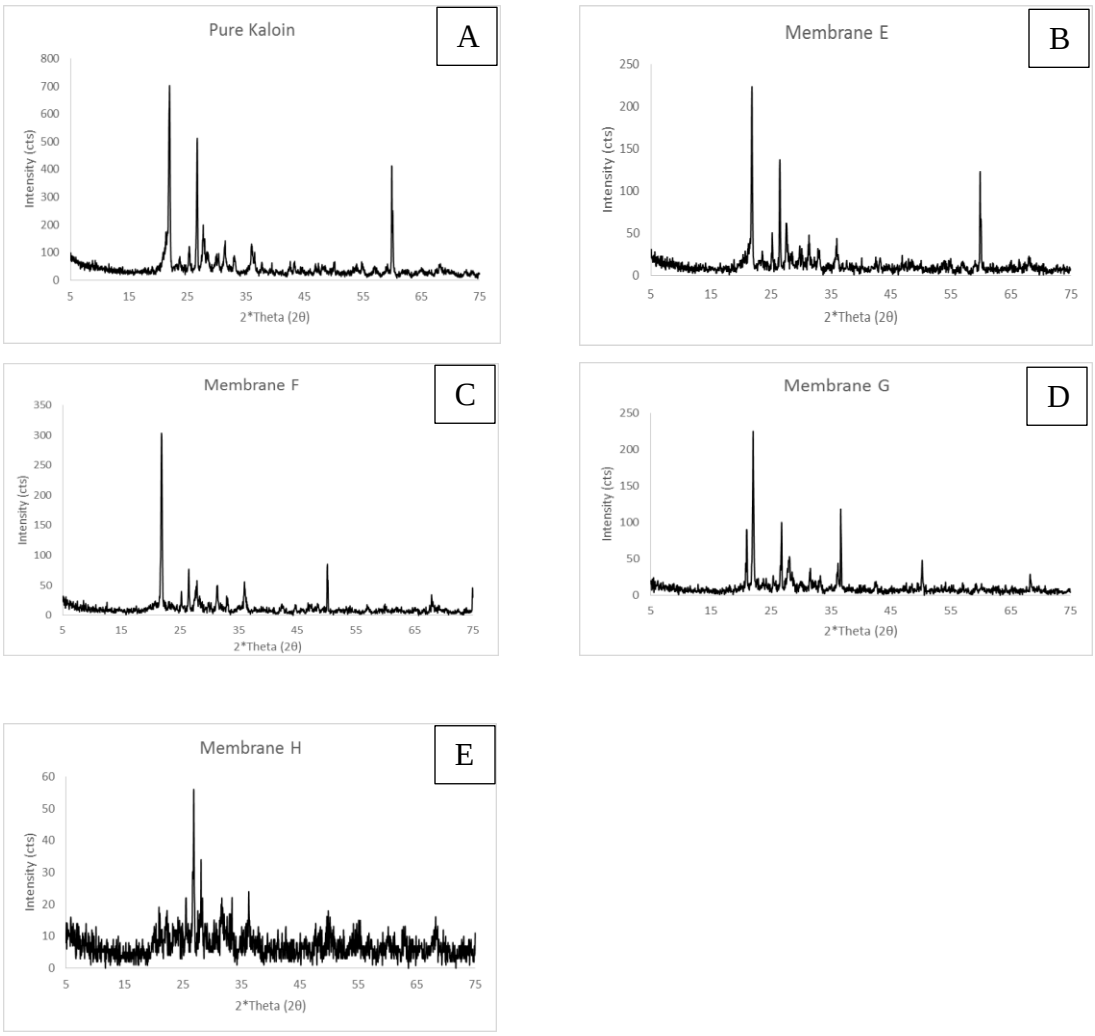

Figure 2: Powder XRD profiles of fabricated membranes [**A**] Pure Kaolin and [**B-E**] Mixture of Kaolin with additives after sintering at 1223 K for 6 hrs

4.3 BET Surface Area Analysis

BET surface area analysis was carried out for Kaolin and important additives using N_2 as the adsorbate gas at 77 K. Although various microscopy images reveal qualitatively about the porous nature of ceramic membranes, but techniques like surface area analysis gives a quantitative estimation of the same. The specific surface area data calculated from surface area measurements has considered the adsorption route of the process within a relative pressure range of approximately 0.05 to 0.35.

For ***Boric Acid*** (Figure 4.3 (A)) the specific surface area is found to be *ca*. 1.532 $m^2 g^{-1}$.

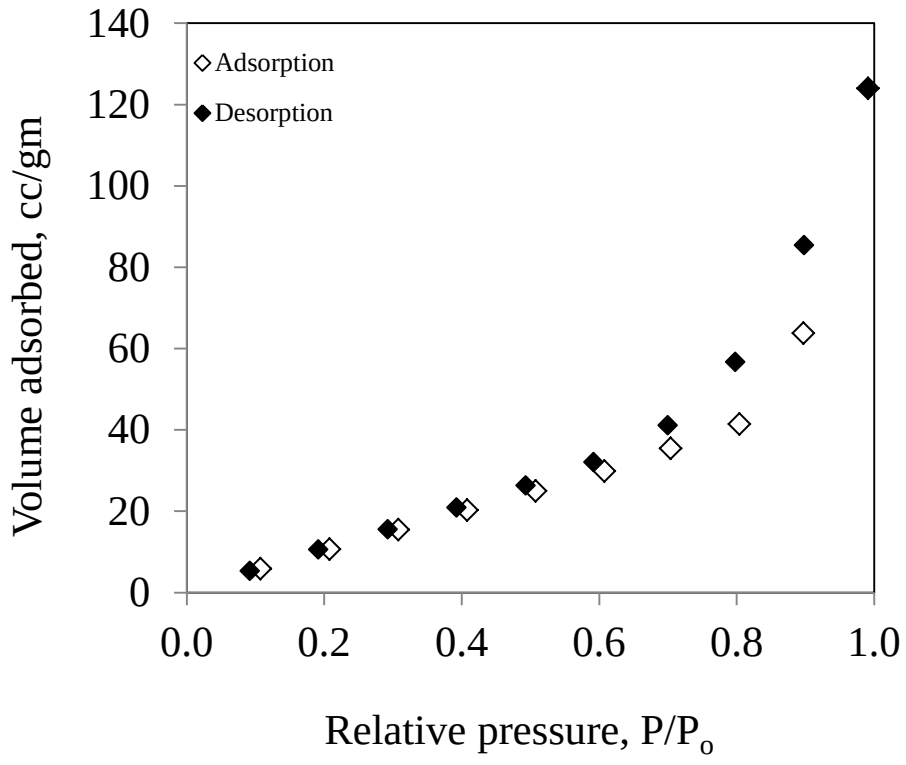

Figure 4.3: (A) BET isotherm of boric acid

The BET isotherm for ***Kaolin*** is shown in figure 4.3 (B). The surface area is measured to be approximately 6.162 $m^2 g^{-1}$.

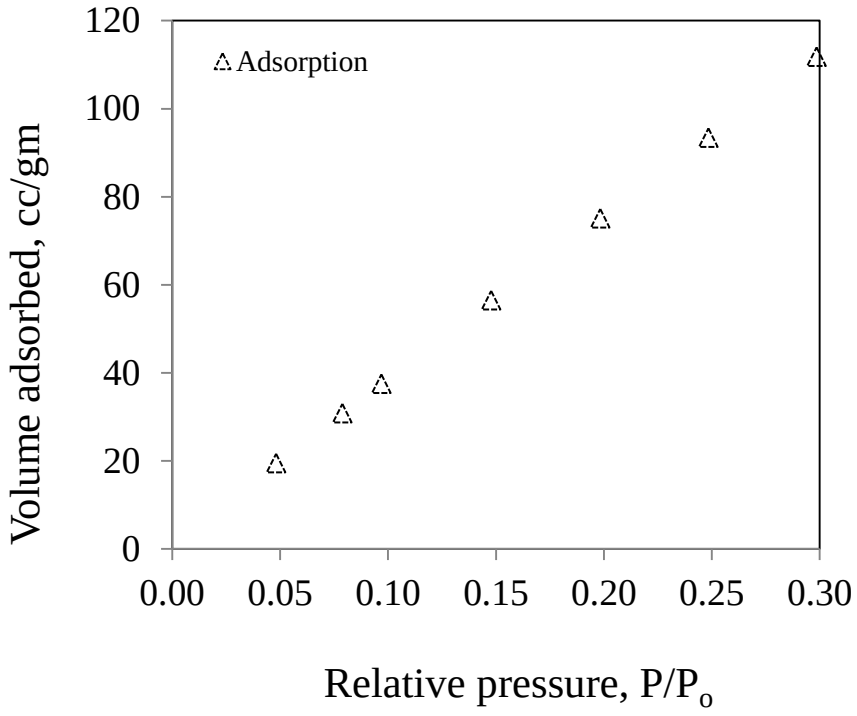

Figure 4.3: (B) BET isotherm of Kaolin

The BET isotherm for ***Sodium Carbonate*** is shown in figure 4.3 (C). The surface area is found to be approximately 4.14 $m^2 g^{-1}$.

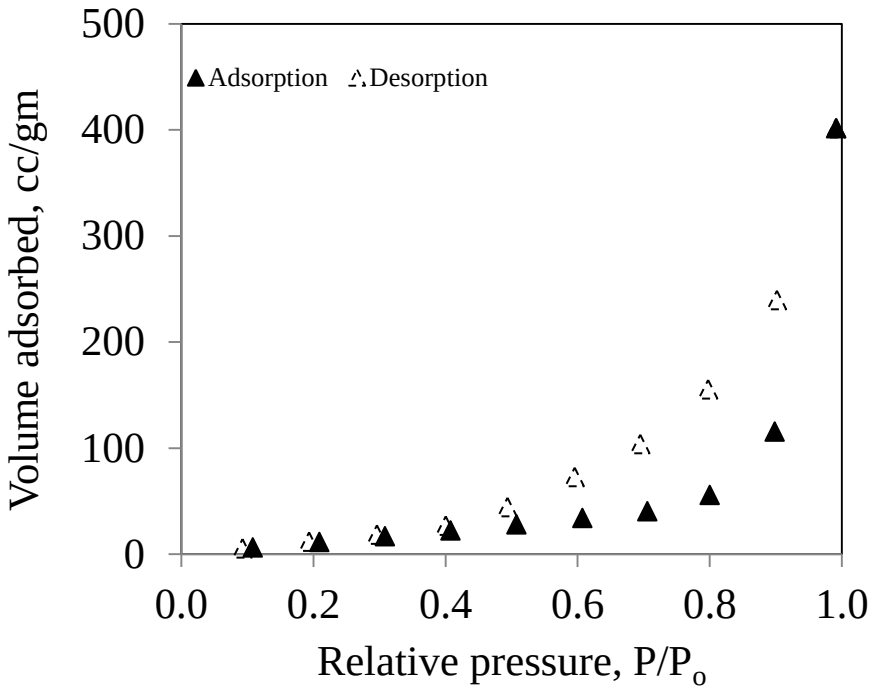

Figure 4.3: (C) BET isotherm of Sodium Carbonate

The BET isotherm for ***Red-Mud*** is shown in figure 4.3 (D). The surface area is found to be approximately 34 m^2 g^{-1}.

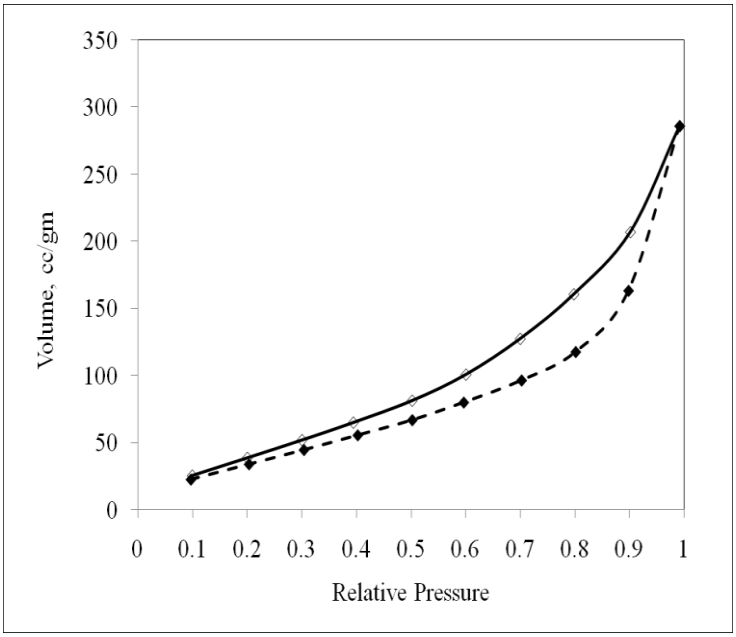

Figure 4.3: (D) BET Isotherm of Red-Mud

Finally, the BET isotherm analysis of membranes F, G and H are carried out. It is seen that of all the fabricated membranes lie within a range from 0.6887 m^2 g^{-1} to 3.554 m^2 g^{-1}. A few interesting observations can be made from the BET analysis:

(a) Since the individual constituents of the membranes don't possess high surface area, hence the finished product too (fabricated membranes) lacks appreciable surface area.

(b) Addition of Red-Mud (with moderate surface area of *ca*. 34 m^2 g^{-1}) improves the surface properties considerably.

(c) Since all individual constituents show hysteresis in the desorption step of the isotherms, it may be concluded that the finished membranes might possesses tortuous pores instead of ideal cylindrical geometry.

4.4 TGA Analysis:

Thermo gravimetric Analysis (TGA) is an analytic method. This measures the change of weight with respect to increase in temperature in a controlled atmosphere and hence predict the thermal stability of the materials. This analysis gives information on absorbed moisture, proportion of organic and inorganic materials in sample, and solvent residue apart from degradation temperature.

In the following figures, the TGA profiles of individual constituents are shown and their degradation temperatures are measured.

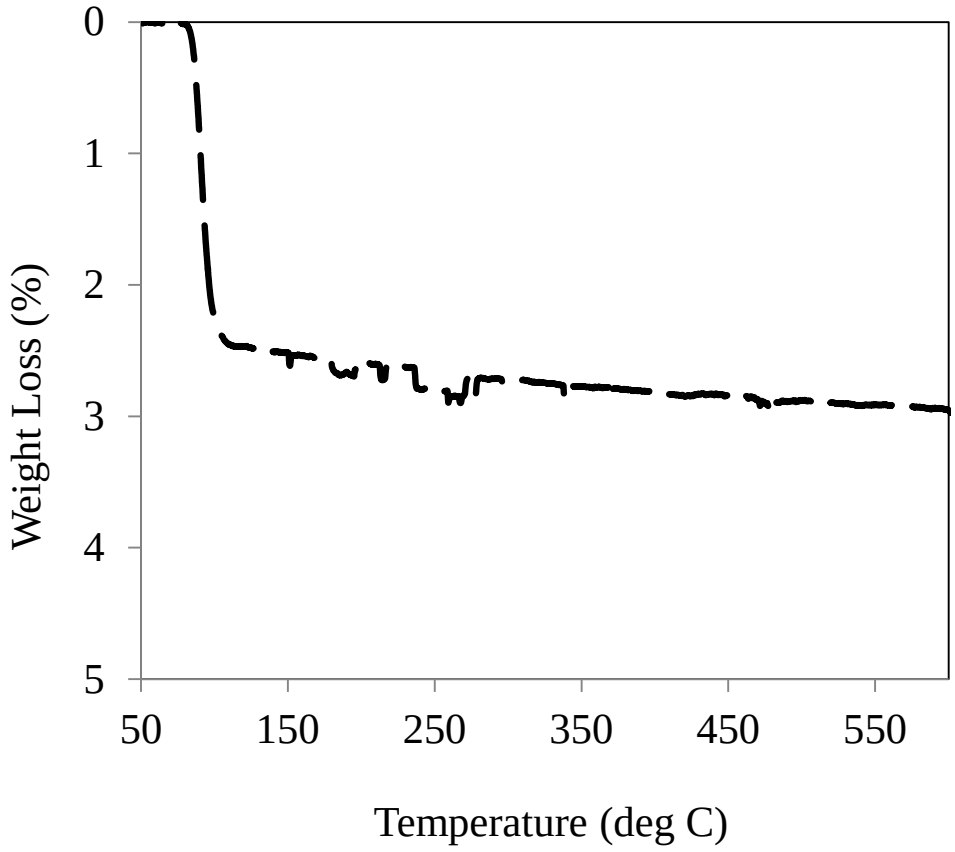

Figure 4.4: (A) TGA analysis of Sodium Carbonate

The TGA profile of sodium carbonate clearly shows 2 different regions. In the first phase between room temperature to 150^{o}C, there is a weight loss of approximately 2.6 %, indicative of removal of moisture and any other volatile material present. From 150^{o}C to 600^{o}C, the horizontal plateau indicates that the weight remains fairly constant throughout without appreciable change.

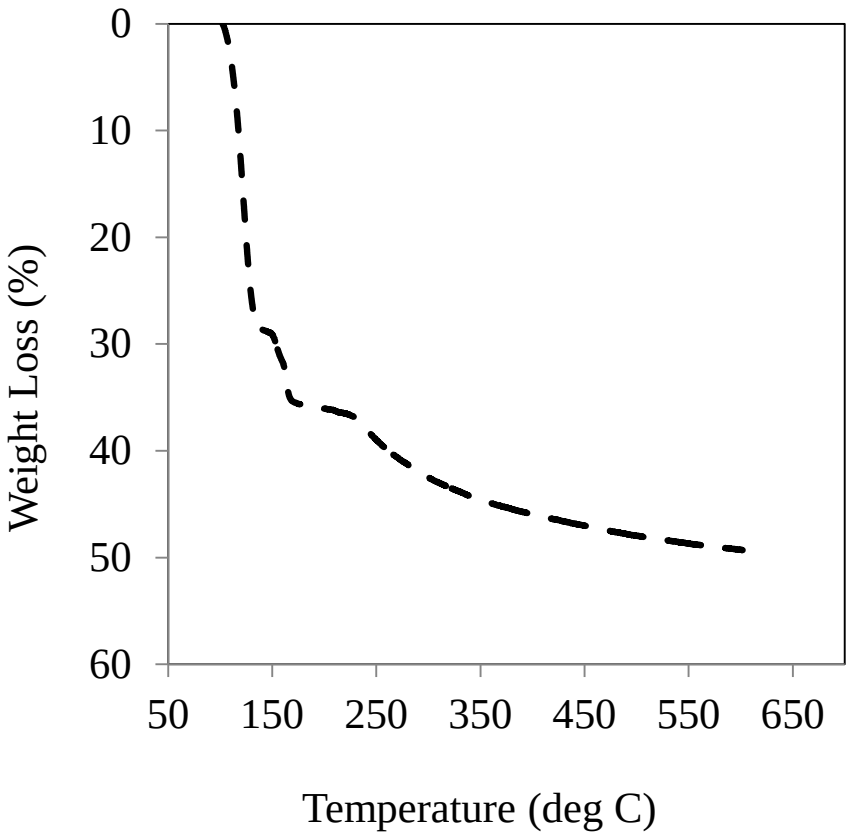

Figure 4.4: (B) TGA analysis of Boric Acid

The TGA profile of boric acid shows a continuous degradation. Between room temperature to 150^{o}C, a weight loss of as high as 35 % indicates that the material is highly hygroscopic in nature and hence high % of moisture is present within the matrix, although, beyond 350^{o}C, the weight loss stabilizes considerably.

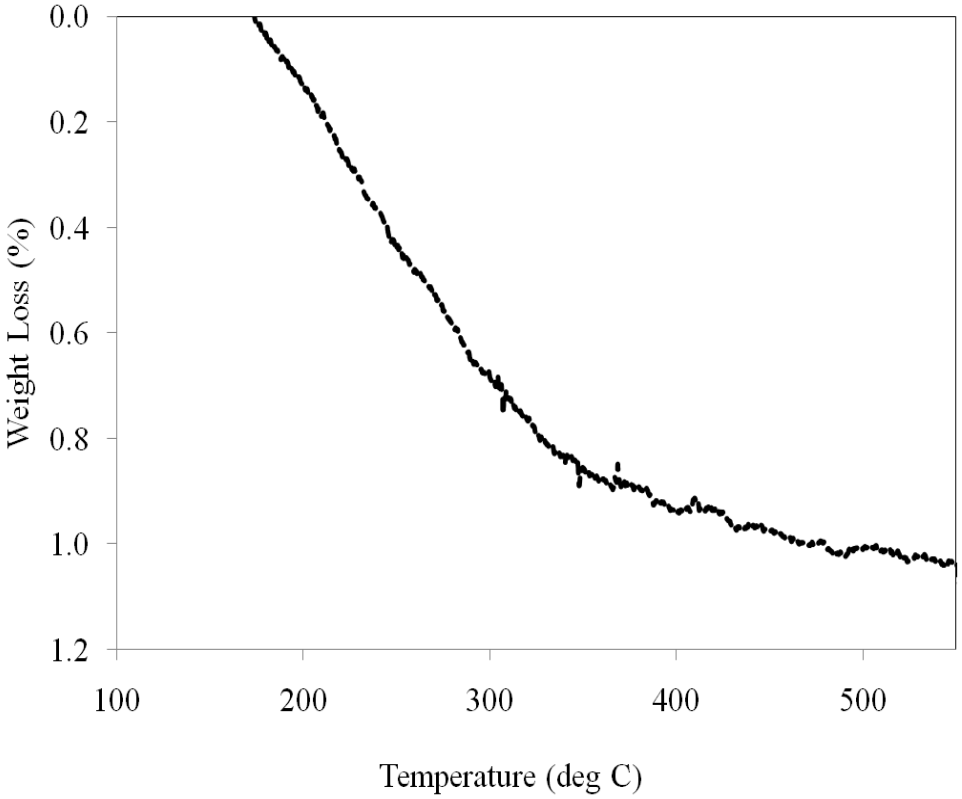

Figure 4.4: (C) TGA analysis of TiO_2

The TGA profile of TiO_2 indicates a fairly stable weight loss profile throughout the course of experimental study. The initial weight loss step of <1% is due to the removal of moisture, which is present in minuscule quantity.

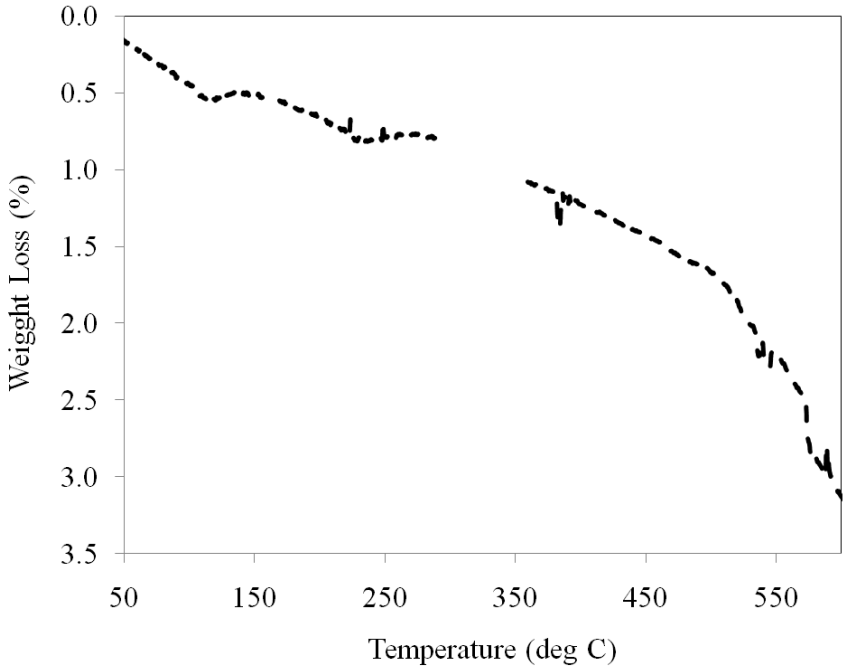

Figure 4.4: (D) TGA analysis of Kaolin

The TGA profile is also similar to that of TiO_2, the only difference is being higher loss in moisture content in the initial stage of the process, indicating hygroscopic nature of this material.

Overall, the TGA profiles indicate that all the ingredients used for membrane fabrication are highly stable at higher temperature and hence, imparts special properties to the finished membrane during the sintering process.

4.5 Characterization of Cu-BTC (or, HKUST-1 or, MOF-199) used as catalyst

Synthesized Cu-BTC was characterized using standard methods *viz*. SEM, Powder XRD. The SEM image is shown in **Figure 4.5**. It clearly shows the crystalline nature of the synthesized samples with average crystal sizes of *ca*. 10 μm or higher.

Figure 4.6 indicates the powder XRD plot of Cu-BTC. The presence of sharp peaks is an indication of crystalline nature of the synthesized material and corroborates well with the SEM images. After matching with the database, no such peak for any impurity is observed, indicating phase purity of the synthesized product.

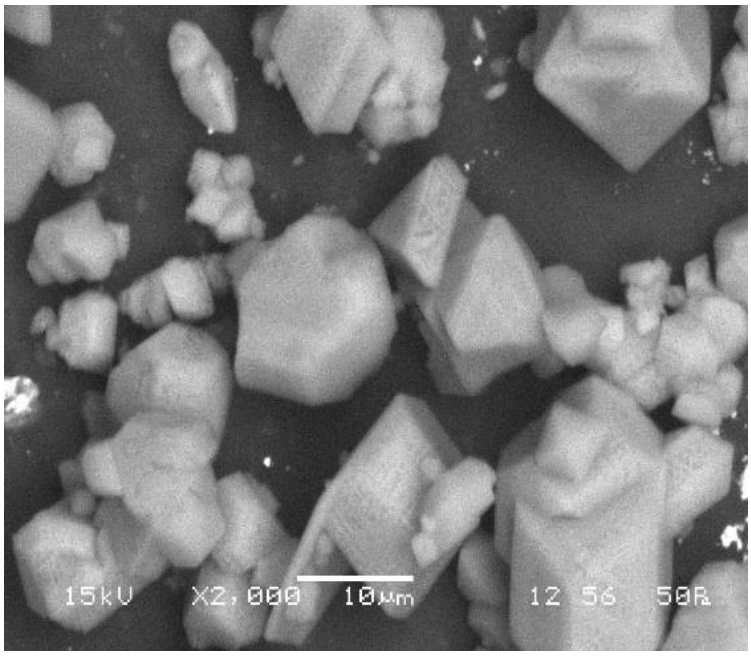

Figure 4.5: SEM images of Cu-BTC (or, HKUST-1 or MOF-199)

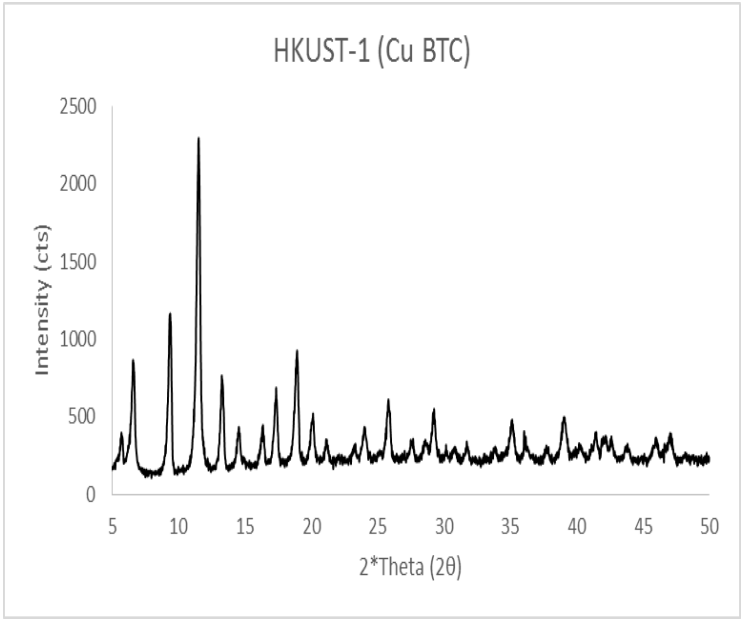

Figure 4.6: Powder XRD plot of Cu-BTC (or, HKUST-1 or MOF-199)

4.6 Permeation Study and recovery of catalyst using Kaolin based Membranes

Owing to superior structural properties of *membranes G and H* in comparison to the rest, they are the preferred membrane chosen for carrying out permeation studies. Hydraulic permeability studies are carried out to find the flux rate through *membranes G and H* (**Figure 4.7)** using methanol. Although the trends are same for both *membranes G and H* with varying slope, *membrane G* shows higher flux rate. The average pore diameter of *membrane G* is found to be 1.32 μm with hydraulic permeability of 1.437×10^{-9} m^3 m^{-2} s^{-1} Pa^{-1}. For *membrane H*, with large average pore diameter of 3.0 μm, hydraulic permeability of 8.382×10^{-10} m^3 m^{-2} s^{-1} Pa^{-1} is measured. A slightly lower value in permeability can be explained due to the occurrence of channeling in *membrane H*.

Since the average pore diameter of both the membranes is less than the average size of the catalysts as is shown in Figure 4.5, both the membranes can be effectively utilized for recovery of Cu-BTC from organic solvents.

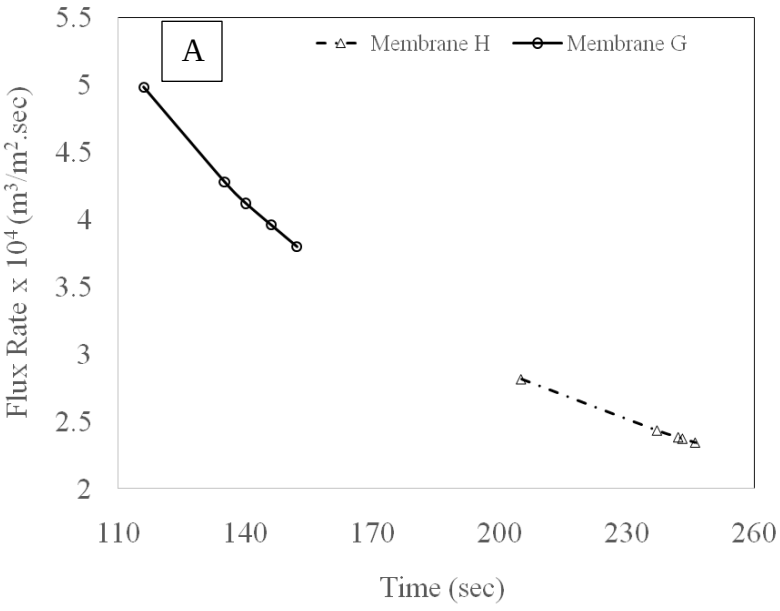

Figure 4.7: **Comparison of flux rates between membranes G & H**

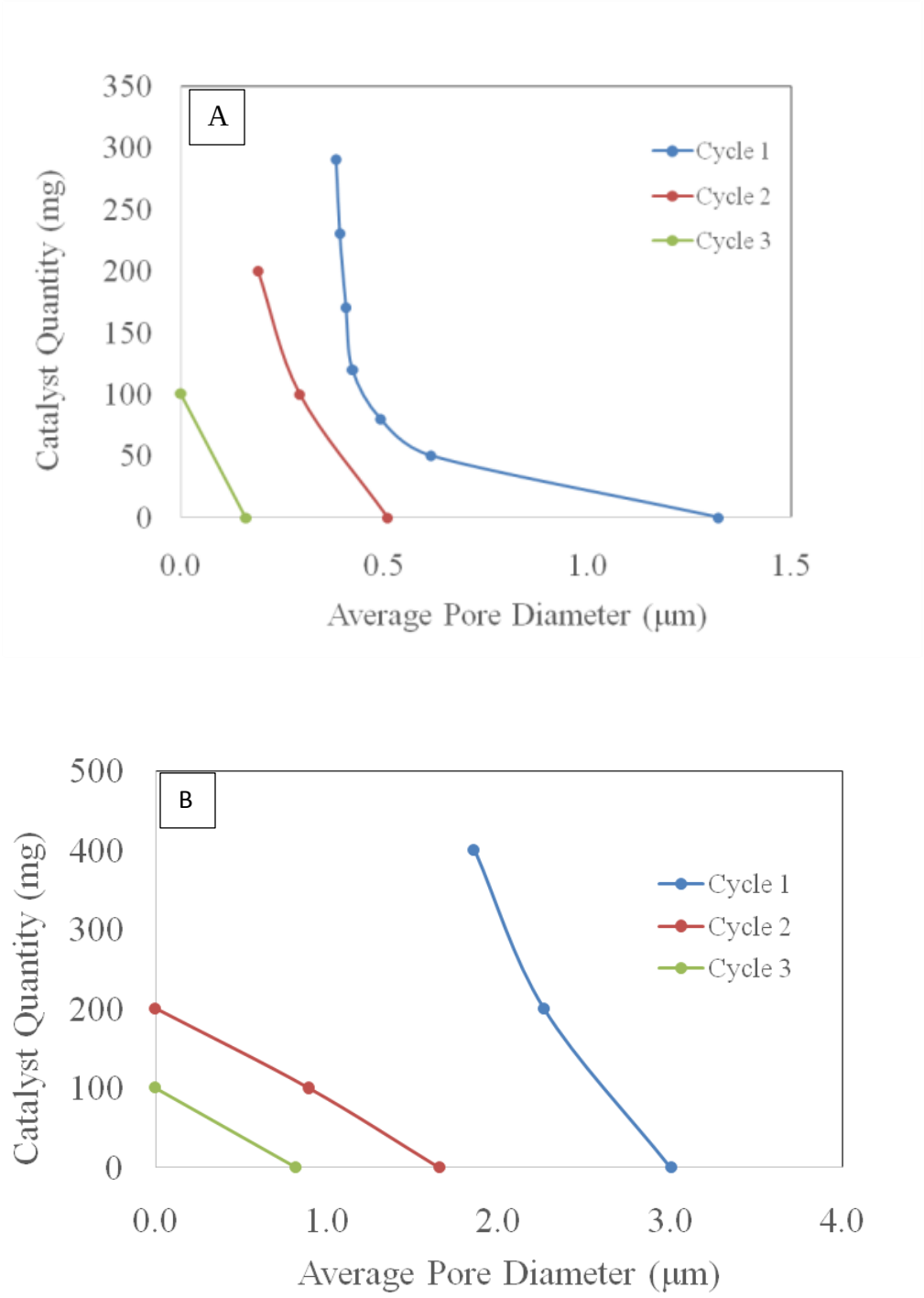

Figure 4.8: (A) & (B) Variation in pore diameter with catalyst loading after different cycles of operation with membranes G & H

Figure 4.8 (A) Blue legend indicates the First cycle. Under this condition, membrane G pores are approximately 1.32 μm in diameter. On addition of catalyst suspension, membrane G pores inherently clogs, leading to reduction in permeate flow and thereby average pore diameter is dropping to 0.38 μm. During Backwash operation, membrane de-fouling occurs and pores are freed and membrane is regenerated resulting in increase in average pore diameter from 0.38 μm to 0.5μm.

Cycle 2 is indicated by **Red legend**. It starts with an average pore diameter of 0.5μm. On addition of catalyst suspension, permeate flow drops, with average pre diameter dropping further to 0.19 μm. Similar regeneration is done by backwash technique. However, there is no significant improvement and the average pore diameter stays as low as 0.16 μm. This could be attributed to improper backwashing due to high pressure drop within the system.

Third cycle is represented in **Green legend**. All active pores are completely clogged, resulting in no permeate flow and on back wash operation it does not lead to significant change in average pore diameter.

Similarly in **Figure 4.8 (B), Blue legend** indicates the First cycle. Under this condition, *membrane H* pore sizes are approximately 3.0 μm in diameter (average). On addition of catalyst suspension, *membrane H* pores inherently clogs leading to reduction in permeate flow and thereby reduction of average pore diameter to 1.85 μm. During Backwash operation, membrane pores are regenerated resulting in slight increase in average pore diameter.

Cycle 2, as indicated by **Red legend,** starts with an average pore diameter of 1.65 μm. On addition of catalyst suspension, permeate flow drops further, due to clogging of the membrane. Similar procedure on regeneration of membrane is undertaken. However, the pore diameter after cycle 2 stands at *ca*. 0.81 μm.

Third cycle is represented by **Green** legend. Active pores are completely clogged during this step, resulting in no permeate flow and on back wash operation it does not lead to significant change in average pore diameter.

From the above observations and analysis it can clearly be inferred that the membrane back washing operations play very much important role in regeneration of active membrane pores.

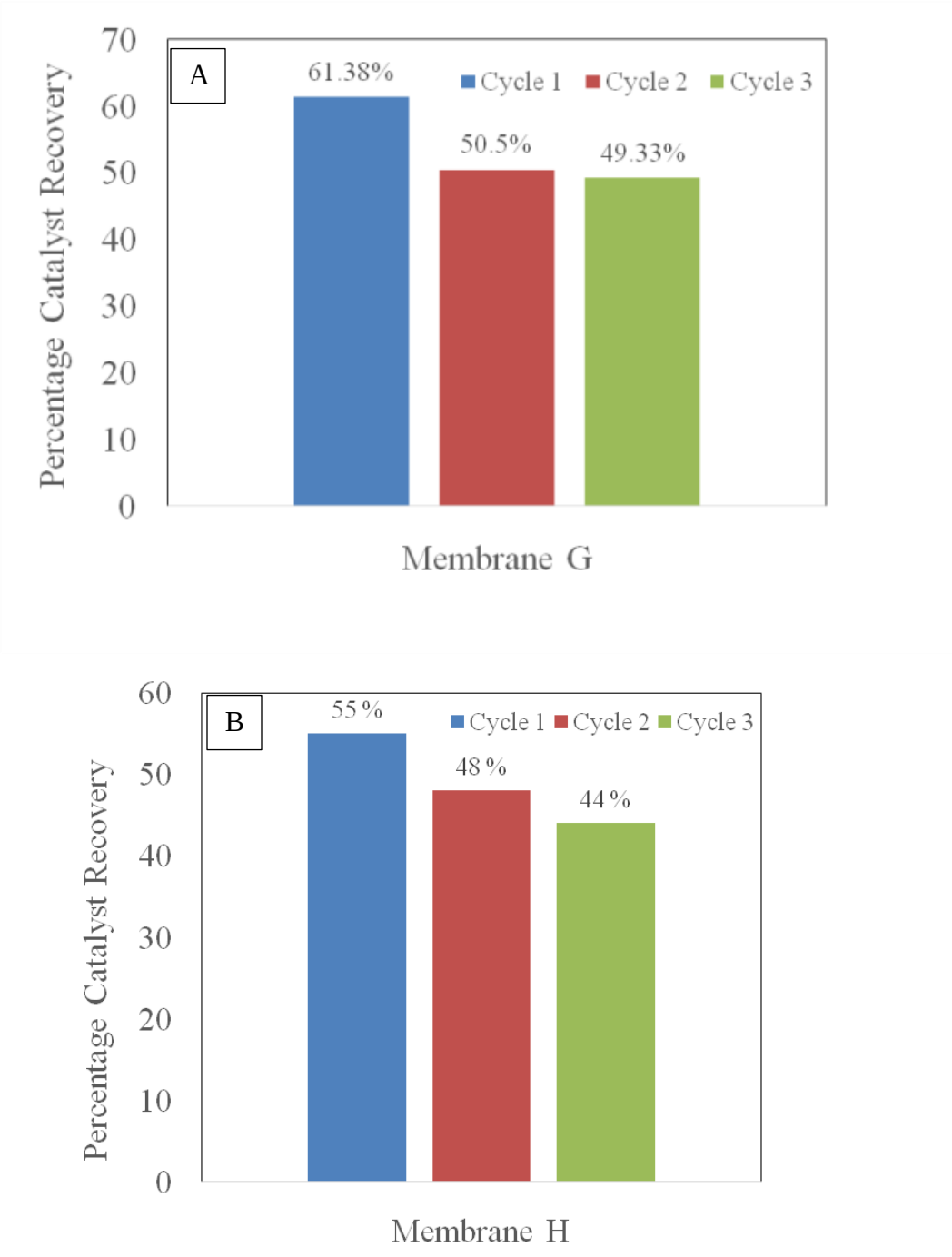

Figure 4.9: Catalyst recovery percentages after different cycles with membranes G & H

Figure 4.9 (A) and (B) summarizes the catalyst recovery by *membranes G and H* respectively after various cycles. *Membrane G* gives a better recover percentage owing smaller average pore diameter in comparison to *membrane H*. The highest recovery of *ca*. 61% is measured for *membrane G* and the value stands at ca. 55% for *membrane H*.

All measured experimental data are tabulated and is shown in the *appendix A*.

5. CONCLUSIONS AND FUTURE SCOPE

In this project work, Kaolin was the primary raw material for membrane fabrication. Various additives/binders were also used based on their suitability and effectiveness in imparting special properties e.g. *mechanical strength and dispersion properties for homogeneity* to the final or finished membrane. A range of additives were used in this work and it included *boric acid, sodium metasilicate, sodium carbonate, calcium carbonate and quartz powder*. Apart from that red-mud and TiO_2 was also used to enhance the *mechanical strength* of the membrane. During membrane preparation with various stoichiometric compositions of ingredients, it was observed that higher percentages of kaolin didn't result into membranes with good flexural strength whereas increasing the % of red-mud enhanced the mechanical strength quite considerably e.g. 10.11 MPa (*membrane F*), 18.93 MPa (*membrane G*) and 12.04 MPa (*membrane H*) respectively. Water permeation studies showed that the average steady state flux was highest for *membrane G* (*ca*. 4.23×10^{-4} m^3 m^{-2} sec^{-1}). The fabricated membranes were successfully characterized using standard procedures like scanning electron microscopy (SEM), field emission SEM, Powder X-ray diffraction analysis, Thermogravimetric analysis and BET surface area analysis to ascertain the membrane morphology both qualitatively as well as quantitatively. The fabricated membranes were undergone catalyst recovery study in a batch membrane module. In this work, Cu-BTC (or, HKUST-1 or, MOF-199), a well known Metal Organic Framework (MOF) was selected as the potential catalyst based upon its superior physical properties like high surface area (*ca*. 1500 m^2 gm^{-1}) and thermal and chemical stability (*under organic medium*). Several cycles (or batches) were carried out inside the membrane module and it was observed that *membrane G* performed better than the rest and a recovery percentage of *ca*. 61% was noted after 3 cycles before the membrane pores were completely choked. Membrane de-fouling and regeneration studies were carried out in detail using back-washing treatment inside the module itself and ultra-sonication techniques for preparing the membranes for next round of operations.

This present work can be extended to study various other aspects of separation science and technology. A few possibilities are included below:

(a) To develop a continuous process to study the catalyst recovery process where various other catalysts can be chosen for recovery used in heterogeneous liquid phase reactions.

(b) Composite ceramic membranes using various other cheap sources of raw materials e.g. *fly ash, drill mud* etc. can be developed which can withstand high temperature and harsh chemical environments.

(c) Within the ambit of present study itself, heavy metal separation, crude oil-water separation; bacterial broth separation can be studied.

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APPENDIX A

Table A.1: Permeation data with methanol solvent using membrane H

Sl. no	Volume (ml)	Time(sec) Run 1	Time(sec) Run 2	Time(sec) Run 3	Time(sec) Run 4	Time(sec) Run 5
1	0	0	0	0	0	0
2	20	40	47	51	51	51
3	40	81	91	103	99	99
4	60	119	143	145	147	144
5	80	161	190	190	195	193
6	100	205	237	242	246	243

Table A.2: Permeation data with methanol solvent using membrane G

Sl. no	Volume (ml)	Time(sec) Run 1	Time(sec) Run 2	Time(sec) Run 3	Time(sec) Run 4	Time(sec) Run 5
1	0	0	0	0	0	0
2	20	23	28	27	25	28
3	40	47	55	51	54	56
4	60	67	80	80	84	85
5	80	90	105	108	116	111
6	100	116	135	140	152	146

Table A.3: Catalyst recovery experiments using Membrane G (Cycle 1)

Sl. no	Volume (ml)	Time(sec) Run 1 (100ml methanol+50 mg catalyst)	Time(sec) Run 2 (100 ml methanol+30 mg catalyst)	Time(sec) Run 3 (100 ml methanol+40 mg catalyst)	Time(sec) Run 4 (100ml methanol+50 mg catalyst)	Time(sec) Run 5 (100ml methanol+60 mg catalyst)
1	0	0	0	0	0	0
2	20	158	183	262	272	292
3	40	280	375	534	560	602
4	60	390	579	796	860	910
5	80	503	790	1068	1150	1242
6	100	619	999	1358	1497	1679

Table A.4: Permeation Experiment with methanol after cycle 1 (membrane G) to study membrane fouling

Sl. no	Volume (ml)	Time (sec)
1	0	0
2	20	296
3	40	497
4	60	641
5	80	773
6	100	924

Table A.5: Catalyst recovery experiments using Membrane G (Cycle 2)

Sl. no	Volume (ml)	Time(sec) Run 1 (100ml methanol+100 mg catalyst)	Time(sec) Run 2 (100ml methanol+100 mg catalyst)	Time (sec) Run 3 (100 ml+70mg catalyst)
1	0	0	0	No permeate
2	20	356	795	No permeate
3	40	765	1953	No permeate
4	60	1336	3250	No permeate
5	80	2005	4754	No permeate
6	100	2772	6516	No permeate

Table A.6: Permeation Experiment with methanol after cycle 2 (membrane G) to study membrane fouling

Sl. no.	Volume(ml)	Time(sec)
1	0	0
2	20	1228
3	40	2908
4	60	4806
5	80	6966
6	100	9378

Table A.7: Permeation Experiment with methanol after cycle 3 (membrane G) to study membrane fouling

Sl. no.	Volume (ml)	Time (sec)
1	0	0
2	20	1528
3	40	3208
4	60	5106
5	80	7500
6	100	9869

Table A.8: Catalyst recovery experiments using Membrane H (Cycle 1)

Sl. no.	Volume (ml)	Time(sec) Run1 (100mlmethanol+200 mg catalyst)	Time(sec) Run 2 (100ml methanol+200 mg catalyst)	Time(sec) Run 3 (100ml methanol+200mg catalyst)
1	0	0	0	No permeate
2	20	70	95	No permeate
3	40	150	205	No permeate
4	60	240	333	No permeate
5	80	323	489	No permeate
6	100	412	612	No permeate

Table A.9: Permeation Experiment with methanol after cycle 1 (membrane H) to study membrane fouling

Sl. no.	Volume (ml)	Time (sec)
1	0	0
2	20	130
3	40	275
4	60	441
5	80	606
6	100	774

Table A.10: Catalyst recovery experiments using Membrane H (Cycle 2)

Sl. no.	Volume (ml)	Time(sec) Run1 (100mlmethanol+200 mg catalyst)	Time(sec) Run 2 (100ml methanol+200mg catalyst)
1	0	0	No permeate
2	20	450	No permeate
3	40	963	No permeate
4	60	1482	No permeate
5	80	2011	No permeate
6	100	2657	No permeate

Table A.11: Permeation Experiment with methanol after cycle 2 (membrane H) to study membrane fouling

Sl. no.	Volume (ml)	Time (sec)
1	0	0
2	20	609
3	40	1234
4	60	1887
5	80	2515
6	100	3168

Table A.12: Permeation Experiment with methanol after cycle 3 (membrane H) to study membrane fouling

Sl. no.	Volume (ml)	Time (sec)
1	0	0
2	20	609
3	40	1234
4	60	1887
5	80	2515
6	100	3168